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<b>(21) International Application Number:</b> PCT/US97/09900 <b>(22) International Filing Date:</b> 6 June 1997 (06.06.97) <b>(30) Priority Data:</b> 60/019,413 7 June 1996 (07.06.96) US <b>(71) Applicant:</b> CHEVRON U.S.A. INC. [US/US]; 555 Market Street, San Francisco, CA 94105 (US). <b>(72) Inventors:</b> ZONES, Stacey, I.; 1874 9th Avenue, San Francisco, CA 94122-4704 (US). CHEN, Cong-Yan; 176 Schooner Court, Richmond, CA 94804 (US). <b>(74) Agents:</b> SHERIDAN, Richard, J. et al.; Chevron Corporation, Law Department, P.O. Box 7141, San Francisco, CA 94120-7141 (US).		<b>(81) Designated States:</b> AL, AM, AT, AU, AZ, BB, BG, BR, BY, CA, CH, CN, CZ, DE, DK, EE, ES, FI, GB, GE, HU, IL, IS, JP, KE, KG, KP, KR, KZ, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, TJ, TM, TR, TT, UA, UG, UZ, VN, ARIPO patent (GH, KE, LS, MW, SD, SZ, UG), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).  <b>Published</b> <i>Without international search report and to be republished upon receipt of that report.</i>
<b>(54) Title:</b> ZEOLITE Me-UTD-1  <b>(57) Abstract</b>  An aluminosilicate zeolite is disclosed which has a silica/alumina mole ratio of about 500 or less and pores with at least one cross-sectional dimension greater than 7.5 Angstroms. Also disclosed is a zeolite comprising a first oxide selected from the group consisting of silicon oxide, germanium oxide and mixtures thereof and a second oxide selected from the group consisting of aluminum oxide, gallium oxide, iron oxide, indium oxide and mixtures of aluminum oxide, boron oxide, gallium oxide, iron oxide, indium oxide, titanium oxide, and vanadium oxide, the zeolite having, after calcination, the X-ray diffraction lines of Table I, and having a mole ratio of the first oxide to the second oxide of about 500 or less. The zeolites are useful in catalysts for hydrocarbon conversion reactions.		

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01 ZEOLITE Me-UTD-1

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BACKGROUND OF THE INVENTION

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Field of the Invention

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SUMMARY OF THE INVENTION

The present invention is directed to a family of crystalline molecular sieves with unique properties, referred to herein as "zeolite Me-UTD-1" or simply "Me-UTD-1".

The designation "Me-UTD-1" is used to indicate that the zeolite has the crystal structure of the UTD-1 disclosed in U.S. Patent No. 5,489,424, but contains atoms other than silicon and oxygen, preferably a metal ("Me") such as aluminum, in the

01 crystal framework. Preferably Me-UTD-1 is obtained in its aluminosilicate form. As  
02 used herein the term "aluminosilicate" refers to a zeolite containing oxides of both  
03 aluminum and silicon in the framework.

04 In accordance with the present invention, there is provided an aluminosilicate  
05 zeolite having a silica/alumina mole ratio of about 500 or less and having pores with at  
06 least one cross-sectional dimension greater than 7.5 Angstroms, preferably at least  
07 about 8 Angstroms. The calcined zeolite has the X-ray diffraction lines of Table I.

08 Further in accordance with this invention there is provided a zeolite comprising  
09 a first oxide selected from the group consisting of silicon oxide, germanium oxide and  
10 mixtures thereof and a second oxide selected from the group consisting of aluminum  
11 oxide, gallium oxide, iron oxide, indium oxide and mixtures of aluminum oxide, boron  
12 oxide, gallium oxide, iron oxide, indium oxide, titanium oxide, and vanadium oxide,  
13 said zeolite having, after calcination, the X-ray diffraction lines of Table I, and having a  
14 mole ratio of the first oxide to the second oxide of about 500 or less. The present  
15 invention also includes this zeolite which is predominantly in the hydrogen form, which  
16 hydrogen form is prepared by ion exchanging with an acid or with a solution of an  
17 ammonium salt followed by a second calcination. Further provided is this zeolite made  
18 substantially free of acidity by neutralizing said zeolite with a basic metal.

19 Also provided in accordance with the present invention is a method of preparing a  
20 boron-containing zeolite comprising oxides of born and silica, said zeolite having, after  
21 calcination, the X-ray diffraction lines of Table I, said method comprising:

22 (a) preparing an aqueous solution containing calcined boron-containing  
23 Beta zeolite, an alkali metal or alkaline earth metal cation, and a  
24 bis(pentamethylcyclopentadienyl) cobalt (III) ion having an anionic counterion which is  
25 not detrimental to the formation of the boron-containing zeolite;

26 (b) maintaining the aqueous solution under conditions sufficient to form  
27 crystals of the boron-containing zeolite; and

28 (c) recovering crystals of the boron-containing zeolite.

29 The present invention additionally provides a process for converting  
30 hydrocarbons comprising contacting a hydrocarbonaceous feed at hydrocarbon  
31  
32  
33  
34

01 converting conditions with a catalyst comprising the Me-UTD-1 zeolite of this  
02 invention, preferably predominantly in the hydrogen form.

03 Further provided by the present invention is a hydrocracking process  
04 comprising contacting a hydrocarbon feedstock under hydrocracking conditions with a  
05 catalyst comprising the Me-UTD-1 of this invention, preferably predominantly in the  
06 hydrogen form.  
07

08 This invention also includes a dewaxing process comprising contacting a  
09 hydrocarbon feedstock under dewaxing conditions with a catalyst comprising the  
10 Me-UTD-1 of this invention, preferably predominantly in the hydrogen form.  
11

12 This invention also includes a process for improving the viscosity index of the  
13 dewaxed product of waxy hydrocarbon feeds comprising contacting the waxy  
14 hydrocarbon feed under isomerization dewaxing conditions with a catalyst comprising  
15 the Me-UTD-1 of this invention, preferably predominantly in the hydrogen form.  
16

17 Also provided by this invention is a process for producing a C<sub>20+</sub> lube oil from a  
18 C<sub>20+</sub> olefin feed comprising isomerizing said olefin feed over a catalyst comprising at  
19 least one Group VIII metal and the Me-UTD-1 of this invention, preferably  
20 predominantly in the hydrogen form.

21 Further provided in accordance with the present invention is a process for  
22 catalytically dewaxing a hydrocarbon oil feedstock boiling above about 350°F and  
23 containing straight chain and slightly branched chain hydrocarbons comprising  
24 contacting said hydrocarbon oil feedstock in the presence of added hydrogen gas at a  
25 hydrogen pressure of about 15-3000 psi with a catalyst comprising at least one Group  
26 VIII metal and the Me-UTD-1 of this invention, preferably predominantly in the  
27 hydrogen form. Also provided is such a process wherein said catalyst comprises a  
28 layered catalyst comprising a first layer comprising at least one Group VIII metal and  
29 the Me-UTD-1 of this invention, and a second layer comprising an aluminosilicate  
30 zeolite which is more shape selective than the zeolite of said first layer.  
31

32 The present invention also provides a process for preparing a lubricating oil  
33 which comprises:  
34

hydrocracking in a hydrocracking zone a hydrocarbonaceous feedstock to obtain an  
effluent comprising a hydrocracked oil, and catalytically dewaxing said effluent

01 comprising hydrocracked oil at a temperature of at least about 400°F and at a pressure  
02 of from about 15 psig to about 3000 psig in the presence of added hydrogen gas with a  
03 catalyst comprising at least one Group VIII metal and the Me-UTD-1 of this invention,  
04 preferably predominantly in the hydrogen form.  
05

06 Further provided is a process for isomerization dewaxing a raffinate comprising  
07 contacting said raffinate in the presence of added hydrogen with a catalyst comprising  
08 at least one Group VIII metal and the Me-UTD-1 of this invention, preferably  
09 predominantly in the hydrogen form.  
10

11 Also included in this invention is a process for increasing the octane of a  
12 hydrocarbon feedstock to produce a product having an increased aromatics content  
13 comprising contacting a hydrocarbonaceous feedstock which comprises normal and  
14 slightly branched hydrocarbons having a boiling range above about 40°C and less than  
15 about 200°C, under aromatic conversion conditions with a catalyst comprising the Me-  
16 UTD-1 of this invention, preferably made substantially free of acidity by neutralizing  
17 said zeolite with a basic metal. Also provided in this invention is such a process  
18 wherein the zeolite contains a Group VIII metal component.  
19

20 Also provided by the present invention is a catalytic cracking process  
21 comprising contacting a hydrocarbon feedstock in a reaction zone under catalytic  
22 cracking conditions in the absence of added hydrogen with a catalyst comprising the  
23 Me-UTD-1 of this invention, preferably predominantly in the hydrogen form. Also  
24 included in this invention is such a catalytic cracking process wherein the catalyst  
25 additionally comprises a large pore crystalline cracking component.  
26

27 The present invention further provides an isomerizing process for isomerizing  
28 C<sub>4</sub> to C<sub>7</sub> hydrocarbons, comprising contacting a catalyst, comprising at least one  
29 Group VIII metal impregnated on the Me-UTD-1 of this invention, preferably  
30 predominantly in the hydrogen form, with a feed having normal and slightly branched  
31 C<sub>4</sub> to C<sub>7</sub> hydrocarbons under isomerizing conditions. Also provided is such an  
32 isomerization process wherein the catalyst has been calcined in a steam/air mixture at  
33 an elevated temperature after impregnation of the Group VIII metal, preferably  
34 platinum.

01           This invention also provides a process for alkylating an aromatic hydrocarbon  
02           which comprises contacting under alkylation conditions at least a mole excess of an  
03           aromatic hydrocarbon with a C<sub>2</sub> to C<sub>20</sub> olefin under at least partial liquid phase  
04           conditions and in the presence of a catalyst comprising the Me-UTD-1 of this  
05           invention, preferably predominantly in the hydrogen form.  
06

07           This invention additionally provides a process for transalkylating an aromatic  
08           hydrocarbon which comprises contacting under transalkylating conditions an aromatic  
09           hydrocarbon with a polyalkyl aromatic hydrocarbon under at least partial liquid phase  
10           conditions and in the presence of a catalyst comprising the Me-UTD-1 of this  
11           invention, preferably predominantly in the hydrogen form.  
12

13           Further provided by this invention is a process to convert paraffins to aromatics  
14           which comprises contacting paraffins with a catalyst comprising gallium, zinc or a  
15           compound of gallium or zinc and the Me-UTD-1 of this invention, preferably made  
16           substantially free of acidity.  
17

18           Also provided is a process for isomerizing olefins comprising contacting said  
19           olefin under conditions which cause isomerization of the olefin with a catalyst  
20           comprising the Me-UTD-1 of this invention, preferably predominantly in the hydrogen  
21           form.  
22

23           Further provided in accordance with this invention is a process for isomerizing  
24           an isomerization feed comprising an aromatic C<sub>8</sub> stream of xylene isomers or mixtures  
25           of xylene isomers and ethylbenzene, wherein a more nearly equilibrium ratio of ortho-,  
26           meta and para-xylenes is obtained, said process comprising contacting said feed under  
27           isomerization conditions with a catalyst comprising the Me-UTD-1 of this invention,  
28           preferably predominantly in the hydrogen form.  
29

30           The present invention further provides a process for oligomerizing olefins  
31           comprising contacting an olefin feed under oligomerization conditions with a catalyst  
32           comprising the Me-UTD-1 of this invention, preferably predominantly in the hydrogen  
33           form.  
34

          This invention also provides a process for converting lower alcohols and other  
          oxygenated hydrocarbons comprising contacting said lower alcohol or other  
          oxygenated hydrocarbon with a catalyst comprising the Me-UTD-1 of this invention,

01 preferably predominantly in the hydrogen form, under conditions to produce liquid  
02 products.

03 Also provided by the present invention is an improved process for the reduction  
04 of oxides of nitrogen contained in a gas stream in the presence of oxygen wherein said  
05 process comprises contacting the gas stream with a zeolite, the improvement  
06 comprising using as the zeolite, the Me-UTD-1 of this invention. The zeolite may  
07 contain a metal or metal ions capable of catalyzing the reduction of the oxides of  
08 nitrogen, and the process may be conducted in the presence of a stoichiometric excess  
09 of oxygen. In a preferred embodiment, the gas stream is the exhaust stream of an  
10 internal combustion engine.  
11  
12

13 This invention also provides a process for converting hydrocarbons comprising  
14 contacting a hydrocarbonaceous feed at hydrocarbon converting conditions with a  
15 catalyst comprising a Group VIII metal and a silica zeolite having, after calcination, the  
16 X-ray diffraction lines of Table IA.  
17

#### 18 DETAILED DESCRIPTION OF THE INVENTION

19 The present invention comprises a family of crystalline, large pore zeolites,  
20 designated "Me-UTD-1". The Me-UTD-1 zeolites have pores which have at least one  
21 cross-sectional dimension which is at least 7.5 Angstroms, preferably at least about 8  
22 Angstroms, more preferably about 8 to about 10 Angstroms. The pores appear to be  
23 in the form of 14 member rings.  
24

25 In preparing Me-UTD-1 zeolites, a bis(pentamethylcyclopentadienyl) cobalt  
26 (III) ion is used as a crystallization template. In general, Me-UTD-1 is prepared by  
27 contacting an active source of silicon oxide and boron oxide (boron-containing Beta  
28 zeolite in its calcined form can be used as the sources of both the silicon oxide and  
29 boron oxide) with the bis(pentamethylcyclopentadienyl) cobalt (III) ion templating  
30 agent (designated as "Q" below) to form the borosilicate form of UTD-1 ("B-UTD-  
31 1"), followed by substitution of the boron in the B-UTD-1 framework with metal  
32 atoms, preferably aluminum.  
33

34 The B-UTD-1 is prepared from a reaction mixture having the composition  
shown in Table A below.



TABLE A

Reaction Mixture

	General	Preferred
Z/Y	0.01 - 0.10	0.06 - 0.08
OH/YO <sub>2</sub>	0.10 - 0.30	0.18 - 0.25
Q/YO <sub>2</sub>	0.05 - 0.30	0.08 - 0.15
M <sub>2x</sub> /YO <sub>2</sub>	0.05 - 0.20	0.08 - 0.12
H <sub>2</sub> O/YO <sub>2</sub>	20 - 100	30 - 60

where Y is selected from the group consisting of silicon, germanium and mixtures thereof; Z represents boron; Q comprises a bis(pentamethylcyclopentadienyl) cobalt (III) ion; M is an alkali or alkaline earth metal cation; and x is the valence of M.

The preferred source of silicon oxide and boron oxide is calcined boron-containing zeolite Beta ("B-Beta"). One advantage of using B-Beta is that it provides B-UTD-1 with very small crystallite size, typically about 2000 Å or less, preferably about 500-1000 Å along the C axis as estimated by TEM.

In practice, B-UTD-1 is prepared by a process comprising:

- (a) preparing an aqueous solution containing calcined B-Beta, an alkali metal or alkaline earth metal cation, and a bis(pentamethylcyclopentadienyl) cobalt (III) ion having an anionic counterion which is not detrimental to the formation of B-UTD-1;
- (b) maintaining the aqueous solution under conditions sufficient to form crystals of B-UTD-1; and
- (c) recovering the crystals of B-UTD-1.

Typically, an alkali metal hydroxide and/or an alkaline earth metal hydroxide, such as the hydroxide of sodium, potassium, lithium, cesium, rubidium, calcium, and magnesium, is used in the reaction mixture; however, this component can be omitted so long as the equivalent basicity is maintained. The templating agent may be used to provide hydroxide ion. Thus, it may be beneficial to ion exchange, for example, the halide for hydroxide ion, thereby reducing or eliminating the alkali metal hydroxide quantity required. The alkali metal cation or alkaline earth cation may be part of the

01 as-synthesized crystalline oxide material, in order to balance valence electron charges  
02 therein.

03 The reaction mixture is maintained at an elevated temperature until the crystals  
04 of the B-UTD-1 zeolite are formed. The hydrothermal crystallization is usually  
05 conducted under autogenous pressure, at a temperature between about 140°C and  
06 170°C. The crystallization period is typically greater than 1 day and preferably from  
07 about 3 days to about 20 days.

08 The zeolite may be prepared with or without mild stirring or agitation.

09 During the hydrothermal crystallization step, the B-UTD-1 crystals can be  
10 allowed to nucleate spontaneously from the reaction mixture. The use of B-UTD-1  
11 crystals as seed material can be advantageous in decreasing the time necessary for  
12 complete crystallization to occur. In addition, seeding can lead to an increased purity  
13 of the product obtained by promoting the nucleation and/or formation of B-UTD-1  
14 over any undesired phases. When used as seeds, B-UTD-1 crystals are added in an  
15 amount between 0.1 and 10% of the weight of silica used in the reaction mixture.

16 Once the zeolite crystals have formed, the solid product is separated from the  
17 reaction mixture by standard mechanical separation techniques such as filtration. The  
18 crystals are water-washed and then dried, e.g., at 90°C to 150°C for from 8 to 24  
19 hours, to obtain the as-synthesized B-UTD-1 zeolite crystals, which, at this point, still  
20 contain some of the bis(pentamethylcyclopentadienyl) cobalt (III) ion template. The  
21 drying step can be performed at atmospheric pressure or under vacuum.

22 B-UTD-1 further has a composition, as synthesized and in the anhydrous state,  
23 in terms of mole ratios, shown in Table B below.

24 TABLE B

25 As-Synthesized B-UTD-1

26	$Y\text{O}_2/Z$	about 50 or greater
27	$M_{2/x}/Y\text{O}_2$	$\leq 0.05$
28	$Q/Y\text{O}_2$	0.01-0.03

29 where Y, Z, M, x and Q are as defined above.

30 The B-UTD-1 can then be treated to remove the cobalt-containing template  
31 and to exchange the boron in the B-UTD-1 framework with another element, e.g.,

01 aluminum. This is typically accomplished in two sequential steps. First, the boron can  
02 be removed from the framework of the B-UTD-1 by treatment with an excess of  
03 protons at pH preferably below 2. A variety of acids, such as HCl, HNO<sub>3</sub> or H<sub>2</sub>SO<sub>4</sub>,  
04 can be used. Components which buffer the system above about pH 3 will slow down  
05 the process. It is helpful to heat these acidic solutions, usually for 1-3 days of reaction  
06 to ensure a greater than 90% removal of the boron.  
07

08 Thus, the B-UTD-1 is typically refluxed in acid, such as 2N HCl until the  
09 cobalt is dissolved. (The solution will turn pink as the cobalt dissolves.) This acid  
10 treatment also removes the boron from the B-UTD-1. When the acid treatment is  
11 finished, the zeolite crystals can be recovered, washed and reheated to about 140°C in  
12 a solution containing a salt of the desired boron-replacing cation or cations. Thus, the  
13 Me-UTD-1 of this invention contains substantially no cobalt, and has at least part of  
14 the boron replaced by another cation or cations.  
15

16 After the cobalt has been removed from the B-UTD-1 and the boron has been  
17 replaced by another element, the resulting Me-UTD-1 has a mole ratio of a first oxide  
18 selected from the group consisting of silicon oxide, germanium oxide and mixtures  
19 thereof to a second oxide selected from the group consisting of aluminum oxide,  
20 gallium oxide, iron oxide, indium oxide and mixtures of aluminum oxide, boron oxide,  
21 gallium oxide, iron oxide, indium oxide, titanium oxide, and vanadium oxide of about  
22 500 or less, preferably about 500 to about 50, more preferably about 200 to about 50.  
23

24 Me-UTD-1 is comprised of a framework structure or topology which is  
25 characterized by its X-ray diffraction pattern. Me-UTD-1 zeolites, in the calcined  
26 form, have a crystalline structure whose X-ray powder diffraction pattern exhibit the  
27 characteristic lines shown in Table I.  
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TABLE I

Calcined Me-UTD-1

<u>2 Theta</u>	<u>d</u>	<u>Relative Intensity <sup>(a)</sup></u>
6.0 ± 0.1	14.4-15.0	VS
7.6 ± 0.1	11.5-11.8	S
14.55 ± 0.15	6.0-6.1	W-M
19.8 ± 0.1	4.4-4.5	M
21.2 ± 0.1	4.17-4.21	VS
22.0 ± 0.1	4.01-4.06	M
22.5 ± 0.1	3.92-3.96	M
24.5 ± 0.05	3.64-3.68	W

<sup>(a)</sup> The X-ray patterns provided are based on a relative intensity scale in which the strongest line in the X-ray pattern is assigned a value of 100; W(weak) is less than 10; M(medium) is between 10 and 40; S(strong) is between 40 and 60; VS(very strong) is greater than 60.

The X-ray powder diffraction pattern for B-UTD-1 also exhibits the characteristic lines shown in Table I.

All-silica UTD-1 zeolite (such as that disclosed in U.S. Patent No. 5,489,424), in the calcined form, has a crystalline structure whose X-ray powder diffraction pattern exhibit the characteristic lines shown in Table IA below.

TABLE IA

Calcined all-silica UTD-1

<u>2 Theta</u>	<u>d</u>	<u>Relative Intensity</u>
6.00 ± 0.05	14.6-14.9	VS
7.60 ± 0.10	11.5-11.8	S-VS
14.5 ± 0.10	6.05-6.15	W-M
18.0 ± 0.10	4.89-4.95	W-M
19.7 ± 0.10	4.48-4.53	W-M

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<u>2 Theta</u>	<u>d</u>	<u>Relative Intensity</u>
21.0 ± 0.10	4.21-4.25	M-S
24.2 ± 0.10	3.66-3.69	W-M
24.95 ± 0.10	3.55-3.58	W-M

1

2       The X-ray powder diffraction patterns were determined by standard techniques.  
3       The radiation was the K-alpha/doublet of copper. The peak heights and the positions,  
4       as a function of  $2\theta$  where  $\theta$  is the Bragg angle, were read from the relative intensities  
5       of the peaks, and  $d$ , the interplanar spacing in Angstroms corresponding to the  
6       recorded lines, can be calculated.

7       Unless otherwise indicated, the variation in the scattering angle (two theta)  
8       measurements, due to instrument error and to differences between individual samples,  
9       is estimated at  $\pm 0.20$  degrees.

10       Representative peaks from the X-ray diffraction pattern of calcined Me-UTD-1  
11       are shown in Table I. Calcination can also result in changes in the intensities of the  
12       peaks as compared to patterns of the "as-made" material, as well as minor shifts in the  
13       diffraction pattern. The zeolite produced by exchanging the metal or other cations  
14       present in the zeolite with various other cations (such as  $H^+$  or  $NH_4^+$ ) yields essentially  
15       the same diffraction pattern, although again, there may be minor shifts in the  
16       interplanar spacing and variations in the relative intensities of the peaks. Minor  
17       variations in the diffraction pattern can result from variations in the silica-to-alumina  
18       (or other oxide) mole ratio of the particular sample due to changes in lattice constants.  
19       In addition, sufficiently small crystals will affect the shape and intensity of peaks,  
20       leading to significant peak broadening. Notwithstanding these minor perturbations, the  
21       basic crystal lattice remains unchanged by these treatments.

22       Crystalline Me-UTD-1 normally will be thermally treated (calcined). Usually, it  
23       is desirable to remove the alkali metal cation by ion exchange and replace it with  
24       hydrogen, ammonium, or any desired metal ion. The zeolite can be leached with  
25       chelating agents, e.g., EDTA or dilute acid solutions, to increase the silica to alumina  
26       (or other oxide) mole ratio. The zeolite can also be steamed; steaming helps stabilize  
27       the crystalline lattice to attack from acids.

01           The zeolite can be used in intimate combination with hydrogenating  
02 components, such as tungsten, vanadium, molybdenum, rhenium, nickel, cobalt,  
03 chromium, manganese, or a noble metal, such as palladium or platinum, for those  
04 applications in which a hydrogenation-dehydrogenation function is desired.  
05

06           Metals may also be introduced into the zeolite by replacing some of the cations  
07 in the zeolite with metal cations via ion exchange techniques. Typical replacing cations  
08 can include metal cations, e.g., rare earth, Group IA, Group IIA and Group VIII  
09 metals, as well as their mixtures. Of the replacing metallic cations, cations of metals  
10 such as rare earth, Mn, Ca, Mg, Zn, Cd, Pt, Pd, Ni, Co, Ti, Al, Sn, and Fe are  
11 particularly preferred.  
12

13           The hydrogen, ammonium, and metal components can be ion-exchanged into  
14 the Me-UTD-1. The zeolite can also be impregnated with the metals, or, the metals  
15 can be physically and intimately admixed with the zeolite using standard methods  
16 known to the art.  
17

18           Typical ion exchange techniques involve contacting the zeolite with a solution  
19 containing a salt of the desired replacing cation or cations. Although a wide variety of  
20 salts can be employed, chlorides and other halides, acetates, nitrates, and sulfates are  
21 particularly preferred. The zeolite is usually calcined prior to the ion-exchange  
22 procedure to remove the organic matter present in the channels and on the surface,  
23 since this results in a more effective ion exchange. Representative ion exchange  
24 techniques are disclosed in a wide variety of patents including U.S. Patent  
25 Nos. 3,140,249 issued on July 7, 1964 to Plank, et al.; 3,140,251 issued on July 7,  
26 1964 to Plank, et al.; and 3,140,253 issued on July 7, 1964 to Plank, et al.  
27

28           Following contact with the salt solution of the desired replacing cation, the  
29 zeolite is typically washed with water and dried at temperatures ranging from 65°C to  
30 about 200°C. After washing, the zeolite can be calcined in air or inert gas at  
31 temperatures ranging from about 200°C to about 800°C for periods of time ranging  
32 from 1 to 48 hours, or more, to produce a catalytically active product especially useful  
33 in hydrocarbon conversion processes.  
34

Me-UTD-1 can be composited with other materials resistant to the temperatures and other conditions employed in organic conversion processes. Such matrix materials include active and inactive materials and synthetic or naturally occurring zeolites as well as inorganic materials such as clays, silica and metal oxides. Examples of such materials and the manner in which they can be used are disclosed in United States Patent No. 4,910,006, issued May 20, 1990 to Zones et al., and U.S. Patent No. 5,316,753, issued May 31, 1994 to Nakagawa, both of which are incorporated by reference herein in their entirety.

Me-UTD-1 zeolites are useful in hydrocarbon conversion reactions. Hydrocarbon conversion reactions are chemical and catalytic processes in which carbon containing compounds are changed to different carbon containing compounds. Examples of hydrocarbon conversion reactions in which Me-UTD-1 are expected to be useful include catalytic cracking, hydrocracking, dewaxing, alkylation, and olefin and aromatics formation reactions. The catalysts are also expected to be useful in other petroleum refining and hydrocarbon conversion reactions such as isomerizing n-paraffins and naphthenes, polymerizing and oligomerizing olefinic or acetylenic compounds such as isobutylene and butene-1, reforming, alkylating (including the alkylation of aromatics with other hydrocarbons), isomerizing polyalkyl substituted aromatics (e.g., m-xylene), and disproportionating aromatics (e.g., toluene) to provide mixtures of benzene, xylenes and higher methylbenzenes and oxidation reactions. Also included are rearrangement reactions to make various naphthalene derivatives. The

1 Me-UTD-1 catalysts have high selectivity, and under hydrocarbon conversion  
2 conditions can provide a high percentage of desired products relative to total products.

3 Me-UTD-1 zeolites can be used in processing hydrocarbonaceous feedstocks.  
4 Hydrocarbonaceous feedstocks contain carbon compounds and can be from many  
5 different sources, such as virgin petroleum fractions, recycle petroleum fractions, shale  
6 oil, liquefied coal, tar sand oil, synthetic paraffins from normal alpha olefins, recycled  
7 plastic feedstocks, and, in general, can be any carbon-containing feedstock susceptible  
8 to zeolitic catalytic reactions. Depending on the type of processing the  
9 hydrocarbonaceous feed is to undergo, the feed can contain metal or be free of metals,  
10 it can also have high or low nitrogen or sulfur impurities. It can be appreciated,  
11 however, that in general processing will be more efficient (and the catalyst more  
12 active) the lower the metal, nitrogen, and sulfur content of the feedstock.

13 For some reactions it is preferred that the Me-UTD-1 have acid sites. For  
14 those reactions, it is preferred that the Me-UTD-1 zeolite be predominantly in its  
15 hydrogen ion form, i.e., it is preferred that, after calcination, at least about 80% of the  
16 cation sites are occupied by hydrogen ions and/or rare earth ions.

17 The conversion of hydrocarbonaceous feeds can take place in any convenient  
18 mode, for example, in fluidized bed, moving bed, or fixed bed reactors depending on  
19 the types of process desired. The formulation of the catalyst particles will vary  
20 depending on the conversion process and method of operation.

21 Other reactions which can be performed using the catalyst of this invention  
22 containing a metal, e.g., a Group VIII metal such platinum, include  
23 hydrogenation-dehydrogenation reactions, denitrogenation and desulfurization  
24 reactions.

25 The following table indicates typical reaction conditions which may be  
26 employed when using catalysts comprising Me-UTD-1 in the hydrocarbon conversion  
27 reactions of this invention. Preferred conditions are indicated in parentheses.

28

Process	Temp., °C	Pressure	LHSV
Hydrocracking	175-485	0.5-350 bar	0.1-30
Dewaxing	200-475	15-3000 psig	0.1-20



Process	Temp., °C	Pressure	LHSV
	(250-450)	(200-3000)	(0.2-10)
Aromatics formation	400-600 (480-550)	atm.-10 bar	0.1-15
Cat. cracking	127-885	subatm. <sup>1</sup> (atm.-5 atm.)	0.5-50
Oligomerization	232-649 <sup>2</sup> 10-232 <sup>4</sup> (27-204) <sup>4</sup>	0.1-50 atm. <sup>2,3</sup> - -	0.2-50 <sup>2</sup> 0.05-20 <sup>5</sup> (0.1-10) <sup>5</sup>
Paraffins to aromatics	100-700	0-1000 psig	0.5-40 <sup>5</sup>
Condensation of alcohols	260-538	0.5-1000 psig	0.5-50 <sup>5</sup>
Isomerization	93-538 (204-315)	50-1000 psig	1-10 (1-4)
Xylene isomerization	260-593 <sup>2</sup> (315-566) <sup>2</sup> 38-371 <sup>4</sup>	0.5-50 atm. <sup>2</sup> (1-5 atm) <sup>2</sup> 1-200 atm. <sup>4</sup>	0.1-100 <sup>5</sup> (0.5-50) <sup>5</sup> 0.5-50

1 <sup>1</sup> Several hundred atmospheres

2 <sup>2</sup> Gas phase reaction

3 <sup>3</sup> Hydrocarbon partial pressure

4 <sup>4</sup> Liquid phase reaction

5 <sup>5</sup> WHSV

6 Other reaction conditions and parameters are provided below.

7 Hydrocracking

8 Using a catalyst which comprises Me-UTD-1 in the hydrogen form and a  
9 hydrogenation promoter, heavy petroleum residual feedstocks, cyclic stocks and other  
10 hydrocrackate charge stocks can be hydrocracked using the process conditions and  
11 catalyst components disclosed in the aforementioned U.S. Patent No. 4,910,006 and  
12 U.S. Patent No. 5,316,753.

17

## 18

23

24

33

34

01 presence of added hydrogen gas at a hydrogen pressure of about 15-3000 psi with a  
02 catalyst comprising Me-UTD-1 and at least one group VIII metal.

03 The Me-UTD-1 hydrodewaxing catalyst may optionally contain a  
04 hydrogenation component of the type commonly employed in dewaxing catalysts. See  
05 the aforementioned U.S. Patent No. 4,910,006 and U.S. Patent No. 5,316,753 for  
06 examples of these hydrogenation components.  
07

08 The hydrogenation component is present in an effective amount to provide an  
09 effective hydrodewaxing and hydroisomerization catalyst preferably in the range of  
10 from about 0.05 to 5% by weight. The catalyst may be run in such a mode to increase  
11 isodewaxing at the expense of cracking reactions.  
12

13 The feed may be hydrocracked, followed by dewaxing. This type of two stage  
14 process and typical hydrocracking conditions are described in U.S. Patent  
15 No. 4,921,594, issued May 1, 1990 to Miller, which is incorporated herein by  
16 reference in its entirety.  
17

18 Me-UTD-1 may also be utilized as a dewaxing catalyst in the form of a layered  
19 catalyst. That is, the catalyst comprises a first layer comprising zeolite Me-UTD-1 and  
20 at least one Group VIII metal, and a second layer comprising an aluminosilicate zeolite  
21 which is more shape selective than zeolite Me-UTD-1. The use of layered catalysts is  
22 disclosed in U.S. Patent No. 5,149,421, issued September 22, 1992 to Miller, which is  
23 incorporated by reference herein in its entirety. The layering may also include a bed of  
24 Me-UTD-1 layered with a non-zeolitic component designed for either hydrocracking  
25 or hydrofinishing.  
26

27 Me-UTD-1 may also be used to dewax raffinates, including bright stock, under  
28 conditions such as those disclosed in U. S. Patent No. 4,181,598, issued January 1,  
29 1980 to Gillespie et al., which is incorporated by reference herein in its entirety.  
30

31 It is often desirable to use mild hydrogenation (sometimes referred to as  
32 hydrofinishing) to produce more stable dewaxed products. The hydrofinishing step  
33 can be performed either before or after the dewaxing step, and preferably after.  
34 Hydrofinishing is typically conducted at temperatures ranging from about 190°C to  
about 340°C at pressures from about 400 psig to about 3000 psig at space velocities  
(LHSV) between about 0.1 and 20 and a hydrogen recycle rate of about 400 to 1500

01 SCF/bbl. The hydrogenation catalyst employed must be active enough not only to  
02 hydrogenate the olefins, diolefins and color bodies which may be present, but also to  
03 reduce the aromatic content. Suitable hydrogenation catalyst are disclosed in U. S.  
04 Patent No. 4,921,594, issued May 1, 1990 to Miller, which is incorporated by  
05 reference herein in its entirety. The hydrofinishing step is beneficial in preparing an  
06 acceptably stable product (e.g., a lubricating oil) since dewaxed products prepared  
07 from hydrocracked stocks tend to be unstable to air and light and tend to form sludges  
08 spontaneously and quickly.

10 Lube oil may be prepared using Me-UTD-1. For example, a C<sub>20+</sub> lube oil may be  
11 made by isomerizing a C<sub>20+</sub> olefin feed over a catalyst comprising Me-UTD-1 in the  
12 hydrogen form and at least one Group VIII metal. Alternatively, the lubricating oil  
13 may be made by hydrocracking in a hydrocracking zone a hydrocarbonaceous  
14 feedstock to obtain an effluent comprising a hydrocracked oil, and catalytically  
15 dewaxing the effluent at a temperature of at least about 400°F and at a pressure of  
16 from about 15 psig to about 3000 psig in the presence of added hydrogen gas with a  
17 catalyst comprising Me-UTD-1 in the hydrogen form and at least one Group VIII  
18 metal.

#### 21 Aromatics Formation

22 Me-UTD-1 can be used to convert light straight run naphthas and similar  
23 mixtures to highly aromatic mixtures. Thus, normal and slightly branched chain  
24 hydrocarbons, preferably having a boiling range above about 40°C and less than about  
25 200°C, can be converted to products having a substantial higher octane aromatics  
26 content by contacting the hydrocarbon feed with a catalyst comprising Me-UTD-1. It  
27 is also possible to convert heavier feeds into BTX or naphthalene derivatives of value  
28 using the catalysts of this invention.

30 The conversion catalyst preferably contains a Group VIII metal compound to  
31 have sufficient activity for commercial use. By Group VIII metal compound as used  
32 herein is meant the metal itself or a compound thereof. The Group VIII noble metals  
33 and their compounds, platinum, palladium, and iridium, or combinations thereof can be  
34 used. Rhenium or tin or a mixture thereof may also be used in conjunction with the  
Group VIII metal compound and preferably a noble metal compound. The most

01 preferred metal is platinum. The amount of Group VIII metal present in the  
02 conversion catalyst should be within the normal range of use in reforming catalysts,  
03 from about 0.05 to 2.0 weight percent, preferably 0.2 to 0.8 weight percent.

04 It is critical to the selective production of aromatics in useful quantities that the  
05 conversion catalyst be substantially free of acidity, for example, by neutralizing the  
06 zeolite with a basic metal, e.g., alkali metal, compound. Methods for rendering the  
07 catalyst free of acidity are known in the art. See the aforementioned U.S. Patent  
08 No. 4,910,006 and U.S. Patent No. 5,316,753 for a description of such methods.

09 The preferred alkali metals are sodium, potassium, and cesium. The zeolite  
10 itself can be substantially free of acidity only at very high silica:alumina mole ratios.

#### 11 Catalytic Cracking

12 Hydrocarbon cracking stocks can be catalytically cracked in the absence of  
13 hydrogen using Me-UTD-1 in the hydrogen form.

14 When Me-UTD-1 is used as a catalytic cracking catalyst in the absence of  
15 hydrogen, the catalyst may be employed in conjunction with traditional cracking  
16 catalysts, e.g., any aluminosilicate heretofore employed as a component in cracking  
17 catalysts. Typically, these are large pore, crystalline aluminosilicates. Examples of  
18 these traditional cracking catalysts are disclosed in the aforementioned U.S. Patent  
19 No. 4,910,006 and U.S. Patent No. 5,316,753. When a traditional cracking catalyst  
20 (TC) component is employed, the relative weight ratio of the TC to the Me-UTD-1 is  
21 generally between about 1:10 and about 500:1, desirably between about 1:10 and  
22 about 200:1, preferably between about 1:2 and about 50:1, and most preferably is  
23 between about 1:1 and about 20:1. The zeolite of this invention and/or the traditional  
24 cracking catalyst may be further ion-exchanged with rare earth ions to modify  
25 selectivity.

26 The cracking catalysts are typically employed with an inorganic oxide matrix  
27 component. See the aforementioned U.S. Patent No. 4,910,006 and U.S. Patent  
28 No. 5,316,753 for examples of such matrix components.

#### 29 Oligomerization

30 It is expected that Me-UTD-1 in the hydrogen form can also be used to  
31 oligomerize straight and branched chain olefins having from about 2 to 21 and  
32

01 preferably 2-5 carbon atoms. The oligomers which are the products of the process are  
02 medium to heavy olefins which are useful for both fuels, i.e., gasoline or a gasoline  
03 blending stock and chemicals.

04 The oligomerization process comprises contacting the olefin feedstock in the  
05 gaseous or liquid phase with a catalyst comprising Me-UTD-1.

06 The zeolite can have the original cations associated therewith replaced by a  
07 wide variety of other cations according to techniques well known in the art. Typical  
08 cations would include hydrogen, ammonium and metal cations including mixtures of  
09 the same. Of the replacing metallic cations, particular preference is given to cations of  
10 metals such as rare earth metals, manganese, calcium, as well as metals of Group II of  
11 the Periodic Table, e.g., zinc, and Group VIII of the Periodic Table, e.g., nickel. One  
12 of the prime requisites is that the zeolite have a fairly low aromatization activity, i.e., in  
13 which the amount of aromatics produced is not more than about 20% by weight. This  
14 is accomplished by using a zeolite with controlled acid activity [alpha value] of from  
15 about 0.1 to about 120, preferably from about 0.1 to about 100, as measured by its  
16 ability to crack n-hexane.

17 Alpha values are defined by a standard test known in the art, e.g., as shown in  
18 U.S. Patent No. 3,960,978 issued on June 1, 1976 to Givens, et al. which is  
19 incorporated totally herein by reference. If required, such zeolites may be obtained by  
20 steaming, by use in a conversion process or by any other method which may occur to  
21 one skilled in this art.

#### 22 Conversion of Paraffins to Aromatics

23 Me-UTD-1 in the hydrogen form can be used to convert light gas C<sub>2</sub>-C<sub>6</sub>  
24 paraffins to higher molecular weight hydrocarbons including aromatic compounds.  
25 Preferably, the zeolite will contain a catalyst metal or metal oxide wherein said metal is  
26 selected from the group consisting of Group IB, IIB, VIII and IIIA of the Periodic  
27 Table. Preferably the metal is gallium, niobium, indium or zinc in the range of from  
28 about 0.05 to 5% by weight.

#### 29 Condensation of Alcohols

30 Me-UTD-1 can be used to condense lower aliphatic alcohols having 1 to 10  
31 carbon atoms to a gasoline boiling point hydrocarbon product comprising mixed  
32  
33  
34

01 aliphatic and aromatic hydrocarbon. The process disclosed in U.S. Patent  
02 No. 3,894,107 issued July 8, 1975 to Butter et al., describes the process conditions  
03 used in this process, which patent is incorporated totally herein by reference.

04 The catalyst may be in the hydrogen form or may be base exchanged or  
05 impregnated to contain ammonium or a metal cation complement, preferably in the  
06 range of from about 0.05 to 5% by weight. The metal cations that may be present  
07 include any of the metals of the Groups I through VIII of the Periodic Table.  
08 However, in the case of Group IA metals, the cation content should in no case be so  
09 large as to effectively inactivate the catalyst, nor should the exchange be such as to  
10 eliminate all acidity. There may be other processes involving treatment of oxygenated  
11 substrates where a basic catalyst is desired.  
12

13  
14 Isomerization

15 The present catalyst is highly active and highly selective for isomerizing C<sub>4</sub> to  
16 C<sub>7</sub> hydrocarbons. The activity means that the catalyst can operate at relatively low  
17 temperature which thermodynamically favors highly branched paraffins. Consequently,  
18 the catalyst can produce a high octane product. The high selectivity means that a  
19 relatively high liquid yield can be achieved when the catalyst is run at a high octane.  
20

21 The present process comprises contacting the isomerization catalyst, i.e., a  
22 catalyst comprising Me-UTD-1 in the hydrogen form, with a hydrocarbon feed under  
23 isomerization conditions. The feed is preferably a light straight run fraction, boiling  
24 within the range of 30°F to 250°F and preferably from 60°F to 200°F. Preferably, the  
25 hydrocarbon feed for the process comprises a substantial amount of C<sub>4</sub> to C<sub>7</sub> normal  
26 and slightly branched low octane hydrocarbons, more preferably C<sub>5</sub> and C<sub>6</sub>  
27 hydrocarbons.  
28

29 It is preferable to carry out the isomerization reaction in the presence of  
30 hydrogen. Preferably, hydrogen is added to give a hydrogen to hydrocarbon ratio  
31 (H<sub>2</sub>/HC) of between 0.5 and 10 H<sub>2</sub>/HC, more preferably between 1 and 8 H<sub>2</sub>/HC. See  
32 the aforementioned U.S. Patent No. 4,910,006 and U.S. Patent No. 5,316,753 for a  
33 further discussion of isomerization process conditions.  
34

A low sulfur feed is especially preferred in the present process. The feed preferably contains less than 10 ppm, more preferably less than 1 ppm, and most

01 preferably less than 0.1 ppm sulfur. In the case of a feed which is not already low in  
02 sulfur, acceptable levels can be reached by hydrogenating the feed in a presaturation  
03 zone with a hydrogenating catalyst which is resistant to sulfur poisoning. See the  
04 aforementioned U.S. Patent No. 4,910,006 and U.S. Patent No. 5,316,753 for a  
05 further discussion of this hydrodesulfurization process.  
06

07 It is preferable to limit the nitrogen level and the water content of the feed.  
08 Catalysts and processes which are suitable for these purposes are known to those  
09 skilled in the art.

10 After a period of operation, the catalyst can become deactivated by sulfur or  
11 coke. See the aforementioned U.S. Patent No. 4,910,006 and U.S. Patent  
12 No. 5,316,753 for a further discussion of methods of removing this sulfur and coke,  
13 and of regenerating the catalyst.  
14

15 The conversion catalyst preferably contains a Group VIII metal compound to  
16 have sufficient activity for commercial use. By Group VIII metal compound as used  
17 herein is meant the metal itself or a compound thereof. The Group VIII noble metals  
18 and their compounds, platinum, palladium, and iridium, or combinations thereof can be  
19 used. Rhenium and tin may also be used in conjunction with the noble metal. The  
20 most preferred metal is platinum. The amount of Group VIII metal present in the  
21 conversion catalyst should be within the normal range of use in isomerizing catalysts,  
22 from about 0.05 to 2.0 weight percent, preferably 0.2 to 0.8 weight percent.  
23  
24

#### 25 Alkylation and Transalkylation

26 Me-UTD-1 can be used in a process for the alkylation or transalkylation of an  
27 aromatic hydrocarbon. The process comprises contacting the aromatic hydrocarbon  
28 with a C<sub>2</sub> to C<sub>16</sub> olefin alkylating agent or a polyalkyl aromatic hydrocarbon  
29 transalkylating agent, under at least partial liquid phase conditions, and in the presence  
30 of a catalyst comprising Me-UTD-1.  
31

32 Me-UTD-1 can also be used for removing benzene from gasoline by alkylating  
33 the benzene as described above and removing the alkylated product from the gasoline.

34 For high catalytic activity, the Me-UTD-1 zeolite should be predominantly in  
its hydrogen ion form. It is preferred that, after calcination, at least about 80% of the  
cation sites are occupied by hydrogen ions and/or rare earth ions.



01           Examples of suitable aromatic hydrocarbon feedstocks which may be alkylated  
02 or transalkylated by the process of the invention include aromatic compounds such as  
03 benzene, toluene and xylene. The preferred aromatic hydrocarbon is benzene. There  
04 may be occasions where naphthalene derivatives may be desirable. Mixtures of  
05 aromatic hydrocarbons may also be employed.

07           Suitable olefins for the alkylation of the aromatic hydrocarbon are those  
08 containing 2 to 20, preferably 2 to 4, carbon atoms, such as ethylene, propylene,  
09 butene-1, trans-butene-2 and cis-butene-2, or mixtures thereof. There may be  
10 instances where pentenes are desirable in this same relationship. The preferred olefins  
11 are ethylene and propylene. Longer chain alpha olefins may be used as well.

13           When transalkylation is desired, the transalkylating agent is a polyalkyl  
14 aromatic hydrocarbon containing two or more alkyl groups that each may have from 2  
15 to about 4 carbon atoms. For example, suitable polyalkyl aromatic hydrocarbons  
16 include di-, tri- and tetra-alkyl aromatic hydrocarbons, such as diethylbenzene,  
17 triethylbenzene, diethylmethylbenzene (diethyltoluene), di-isopropylbenzene,  
18 di-isopropyltoluene, dibutylbenzene, and the like. Preferred polyalkyl aromatic  
19 hydrocarbons are the dialkyl benzenes. A particularly preferred polyalkyl aromatic  
20 hydrocarbon is di-isopropylbenzene.

22           When alkylation is the process conducted, reaction conditions are as follows.  
23 The aromatic hydrocarbon feed should be present in stoichiometric excess. It is  
24 preferred that molar ratio of aromatics to olefins be greater than four-to-one to prevent  
25 rapid catalyst fouling. The reaction temperature may range from 100°F to 600°F,  
26 preferably 250°F to 450°F. The reaction pressure should be sufficient to maintain at  
27 least a partial liquid phase in order to retard catalyst fouling. This is typically 50 psig  
28 to 1000 psig depending on the feedstock and reaction temperature. Contact time may  
29 range from 10 seconds to 10 hours, but is usually from 5 minutes to an hour. The  
30 weight hourly space velocity (WHSV), in terms of grams (pounds) of aromatic  
31 hydrocarbon and olefin per gram (pound) of catalyst per hour, is generally within the  
32 range of about 0.5 to 50.

34           When transalkylation is the process conducted, the molar ratio of aromatic  
hydrocarbon to polyalkyl aromatic hydrocarbon will generally range from about 1:1 to

-24-

01 25:1, and preferably from about 2:1 to 20:1. The reaction temperature may range from  
02 about 100°F to 600°F, but it is preferably about 250°F to 450°F. The reaction  
03 pressure should be sufficient to maintain at least a partial liquid phase, typically in the  
04 range of about 50 psig to 1000 psig, preferably 300 psig to 600 psig. The weight  
05 hourly space velocity will range from about 0.1 to 10. U.S. Patent No. 5,082,990  
06 issued on January 21, 1992 to Hsieh, et al. describes such processes and is  
07 incorporated herein by reference.  
08

09 Xylene Isomerization

10 Me-UTD-1 in the hydrogen form may also be useful in a process for  
11 isomerizing one or more xylene isomers in a C<sub>8</sub> aromatic feed to obtain ortho-, meta-,  
12 and para-xylene in a ratio approaching the equilibrium value. In particular, xylene  
13 isomerization is used in conjunction with a separate process to manufacture para-  
14 xylene. For example, a portion of the para-xylene in a mixed C<sub>8</sub> aromatics stream may  
15 be recovered by crystallization and centrifugation. The mother liquor from the  
16 crystallizer is then reacted under xylene isomerization conditions to restore ortho-,  
17 meta- and para-xylenes to a near equilibrium ratio. At the same time, part of the  
18 ethylbenzene in the mother liquor is converted to xylenes or to products which are  
19 easily separated by filtration. The isomerate is blended with fresh feed and the  
20 combined stream is distilled to remove heavy and light by-products. The resultant C<sub>8</sub>  
21 aromatics stream is then sent to the crystallizer to repeat the cycle.  
22

23 Optionally, isomerization in the vapor phase is conducted in the presence of 3.0  
24 to 30.0 moles of hydrogen per mole of alkylbenzene (e.g., ethylbenzene). If hydrogen  
25 is used, the catalyst should comprise about 0.1 to 2.0 wt% of a  
26 hydrogenation/dehydrogenation component selected from Group VIII (of the Periodic  
27 Table) metal component, especially platinum or nickel. By Group VIII metal  
28 component is meant the metals and their compounds such as oxides and sulfides.  
29

30 Optionally, the isomerization feed may contain 10 to 90 wt% of a diluent such  
31 as toluene, trimethylbenzene, naphthenes or paraffins.  
32  
33  
34

Other Uses for Me-UTD-1

Me-UTD-1 can also be used as an adsorbent with high selectivities based on molecular sieve behavior and also based upon preferential hydrocarbon packing within the pores.

Me-UTD-1 may also be used for the catalytic reduction of the oxides of nitrogen in a gas stream. Typically the gas stream also contains oxygen, often a stoichiometric excess thereof. Also, the Me-UTD-1 may contain a metal or metal ions within or on it which are capable of catalyzing the reduction of the nitrogen oxides. Examples of such metals or metal ions include copper, cobalt and mixtures thereof.

One example of such a process for the catalytic reduction of oxides of nitrogen in the presence of a zeolite is disclosed in U.S. Patent No. 4,297,328, issued October 27, 1981 to Ritscher et al., which is incorporated by reference herein. There, the catalytic process is the combustion of carbon monoxide and hydrocarbons and the catalytic reduction of the oxides of nitrogen contained in a gas stream, such as the exhaust gas from an internal combustion engine. The zeolite used is metal ion-exchanged, doped or loaded sufficiently so as to provide an effective amount of catalytic copper metal or copper ions within or on the zeolite. In addition, the process is conducted in an excess of oxidant, e.g., oxygen.

EXAMPLES

The following examples demonstrate but do not limit the present invention.

Example 1Preparation of Template

Five grams of decamethyl cobalticium hexafluorophosphate (purchased) were dissolved in a warmed solution of 1200 cc ethanol and 800 cc water. This solution was then run through a column of Dowex 50-X8 cation exchange resin (previously washed with 60% ethanol) with the complex sticking to the resin. Next a 50/50 solution of 2N HCl and ethanol (total = 4,500 cc) was run over the exchange resin in a column in order to elute the cobalt complex as a chloride salt. The ethanol portion was stripped off under reduced pressure and at 70°C. The remaining acidic solution

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1 was neutralized with concentrated NaOH. This solution was concentrated down, under  
2 reduced pressure and heating to 800 cc. A threefold extraction was carried out with  
3 chloroform using 400 cc each time. Twenty grams of anhydrous  $\text{MgSO}_4$  was used to  
4 dry the combined extracts and the solution was stripped to dryness to yield the chloride  
5 salt.

6 The recovered chloride salt was then dissolved in 10 cc water and mixed with  
7 20 cc of BioRad AG-1X8 hydroxide exchange resin. The resulting mixture was stirred  
8 overnight, after which the resin was filtered off. The resin was then washed with a  
9 little additional water and a yellow-brown solution was collected which titrated to 0.25  
10 Molar in hydroxide. Additional product was monitored as coming off resin as long as  
11 the yellow color was observed in the elution collection. The color can be used as a  
12 measure of extent of ion-exchange in either of the two exchange steps described.

13

14

#### Example 2

15

#### Synthesis of Borosilicate B-UTD-1

16

17 The synthesis of a small crystal borosilicate B-UTD-1 was carried out by  
18 combining the following amounts of reagents in a Teflon liner for a Parr 125 cc  
19 reactor, and heating for 5 days without stirring at 150°C. Twenty grams of a 0.21 M  
20 solution of the cobaltectium hydroxide template of Example 1 was mixed with 3.7 cc of  
21 1.0N NaOH. Lastly, 2.20 grams of calcined boron beta zeolite was added to supply  
22 both the boron and silicon to the reaction. The product crystallized as clusters of very  
23 small rods, and the XRD pattern was considerably line-broadened compared to the  
24 pure silica version of UTD-1. The crystallite size was estimated by TEM methods to be  
25 about 500-1000 Å along the C axis. The product (which still contained the template)  
26 was analyzed by X-ray diffraction and the results are tabulated in Table II below.

26

TABLE II

27

As-Synthesized B-UTD-1

<u>2 Theta</u>	<u>d</u>	<u>Relative Intensity</u>
5.94	14.9	26
7.46	11.8	33
12.0	7.4	25

SUBSTITUTE SHEET (RULE 26)

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<u>2 Theta</u>	<u>d</u>	<u>Relative Intensity</u>
14.6	6.08	28
18.1	4.90	21
19.4	4.57	30
21.2	4.19	100
22.1	4.02	43
22.5	3.95	28
24.4	3.65	19

1  
2 A very novel and unexpected aspect of this synthesis is that the recovered  
3 reaction filtrate can then be directly reused by simply adding an additional charge of  
4 calcined boron beta zeolite. No additional base need be added and the presence of  
5 dissolved sodium borates does not seem to pose a problem for the crystallization. Of  
6 course, the filtrate must contain sufficient template for the B-UTD-1 to form, but this  
7 reuse of the filtrate allows one to maximize the use of the template. In fact, this  
8 methodology can be employed yet a third time as well. With each reaction the filtrate  
9 pH is lower, and as such it might be expected that reaction crystallization times will  
10 start to lengthen. Once the effective pH of the filtrate drops below about 9, it may not  
11 be possible to reuse it. However, using this method, a very high efficiency for using the  
12 cobaltectium template can be obtained. This is an important discovery in that the  
13 cobaltectium complex is the most expensive component in the system.

14 Thus, the solution remaining from the reaction described above (which still  
15 contained some of the template) was transferred to a new reactor and the same amount  
16 of B-Beta as described above was added to it. The reaction was run as described  
17 above, with the resulting product being B-UTD-1.

18

### 19 Example 3

#### 20 Calcination of B-UTD-1

21 The as-made B-UTD-1 can be calcined to remove the organic material in the  
22 pores. The material was calcined at 60°C increase per hour up to 120°C where it was  
23 held for 2 hours. The atmosphere was nitrogen with a small amount of air being bled

-28-

1 into the flow. Heating was continued at 60°C per hour up to 540°C and the heating  
2 was held at this temperature for 4 hours. The calcination was then taken to 600°C over  
3 2 hours and held at this temperature for another 4 hours before the sample was cooled.  
4 The mass loss was typically 12-15% and a gray-green solid was obtained. The  
5 calcined B-UTD-1 was analyzed by X-ray diffraction and the results are tabulated in  
6 Table III below.

7 TABLE III  
8 Calcined B-UTD-1

<u>2 Theta</u>	<u>d</u>	<u>Relative Intensity</u>
6.09	14.5	94
7.71	11.5	49
14.7	6.04	9
18.3	4.86	12
19.9	4.46	16
20.3	4.37	8
21.3	4.17	100
22.1	4.01	15
22.6	3.92	10
24.4	3.64	9
25.0	3.56	10
26.3	3.39	9
28.4	3.15	9
29.4	3.04	7
32.6	2.75	8

9

10

Example 4

11

## Conversion of B-UTD-1 to Active Acidic Form

12

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14

15

The task of both removing cobalt and converting the high-silica borosilicate  
UTD-1 to its more strongly acidic aluminosilicate form was accomplished in two  
sequential steps. First, the calcined product of Example 3 was refluxed in 2N HCl for  
1-2 days, yielding a pink solution as cobalt was dissolved. The solid was recovered,

01 briefly washed, and then reheated to 140°C in the presence of aluminum nitrate  
02 solution. The proportions to form the solution were 1: 1.1: 10 for zeolite : aluminum  
03 nitrate: water. The heating was carried out in a Teflon lined reactor for 3 days. At this  
04 stage the aluminosilicate had lost no crystallinity. This was also true of a sample  
05 analyzed just after reflux in 2N HCl solution. The aluminosilicate UTD-1 (Al-UTD-1)  
06 was now ready for use in catalytic reactions. The Al-UTD-1 (calcined) was analyzed  
07 and found to have a silica to alumina mole ratio of 88. It was also analyzed by X-ray  
08 diffraction and the results are tabulated in Table IV below.  
09  
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-30-

1 TABLE IV  
2 Al-UTD-1

2 Theta	d	Relative Intensity
5.97	14.8	100
7.60	11.6	53
9.22	9.58	6
12.4	7.11	5
14.4	6.13	7
17.9	4.93	7
19.7	4.49	16
21.1	4.21	79
21.9	4.06	10
22.4	3.96	11
23.2	3.83	6
24.2	3.67	4
25.1	3.55	3
26.0	3.43	5
27.9	3.19	3
29.3	3.05	4
29.8	3.00	5
32.2	2.78	4
35.3	2.54	3
36.7	2.45	4
37.5	2.40	4

3

4

Example 5

5

## Conversion of Methanol Using Al-UTD-1

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7

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9

Al-UTD-1 material was tested as a catalyst for the conversion of methanol to higher hydrocarbons. A Al-UTD-1 sample with only a small amount of Al in the framework was run at 400°C with methanol as feed, delivered by syringe pump, at atmospheric pressure (nitrogen carrier gas) and using a space-velocity of 1.2.



-31-

01 Products from collecting the liquid phase in a cold trap, and subsequent analysis by  
02 GC/MS revealed a range of polymethylated benzenes. Considerable quantities of  
03 pentamethyl and hexamethyl benzene were detected, indicating large-pore zeolite  
04 behavior.  
05

#### 07 Example 6

##### 08 Constraint Index Determination

09 The aluminosilicate AI-UTD-1, typical of product from Example 4, in the  
10 hydrogen form and calcined in air for about four hours at about 540°C was pelleted,  
11 broken and meshed (20-40). About 0.50 gram was loaded into a 3/8 inch stainless  
12 steel tube with alundum on both sides of the zeolite bed. After in-situ drying to about  
13 538°C, the catalyst is cooled down to about 370°C in a flow of helium. A 50/50 feed  
14 of n-hexane and 3-methylpentane was introduced to run a Constraint Index test for the  
15 AI-UTD-1.  
16

17 The feed conversion was 50% for the first sampling, occurring at 10 minutes of  
18 reaction. The catalysts showed gradual fouling with the conversion dropping to 30%  
19 after several hours. However, the C.I. value remained constant over this period,  
20 measuring at 0.2. This is also consistent with a large pore zeolite, showing no steric  
21 preference for cracking the smaller, linear hexane isomer. The C<sub>5</sub> iso/ normal ratio was  
22 near 20 and in the same area as other known large pore zeolites like Zeolite Y or SSZ-  
23 24.  
24

#### 27 Example 7

##### 28 Hydrocracking

29 The AI-UTD-1 was ion-exchanged in solution to give a palladium-containing  
30 zeolite. The exchange solution was buffered with ammonium hydroxide to pH 9.5-  
31 10.5. The palladium salt was the tetraamine dinitrate. The intent was to achieve 0.5  
32 wt.% loading of palladium. The exchange was carried out at room temperature for 3-4  
33 days and, after collection by filtration, followed by washing and drying. The resulting  
34 solids were calcined up to 482°C for a period of 3 hours in air. The pelleted, broken

-32-

01 and meshed material was packed into a reactor and prepared for reaction with  
02 hexadecane under high hydrogen pressures (1200 psi ).

03 At 590°F, and without titration, the conversion was already exceeding 96%.  
04 The proportion of cracking to isomerization behavior was about 2/1. The C<sub>3</sub>+ fraction  
05 over the C<sub>4</sub> was typically greater than 10 times as much.  
06

07

08 Example 8

09 Preparation of Pt/Cs/Al-UTD-1

10 A sample of cesium-neutralized Al-UTD-1 was prepared by suspending 0.67 g  
11 of Al-UTD-1 (prepared as described in Example 4) in 10 g of water. 0.33 Gram of  
12 CsOH solution (containing 66,450 ppm Cs) was added to 5 g water. The resulting  
13 CsOH solution was added to the zeolite slurry with hand shaking, and the hand shaking  
14 continued for another three minutes. The suspension was then placed on a shaker and  
15 shaken at room temperature for 24 hours. The pH value of the suspension was 10.0.  
16

17 The suspension was filtered without washing with water, and the resulting solid  
18 was air dried at room temperature overnight. The resulting solid was calcined in air  
19 with the following temperature program:

- 20
- 21 - from room temperature to 250° F at a heating rate of 1° F/minute,
  - 22 - at 250° F for 16 hours,
  - 23 - from 250° F to 570° F at a heating rate of 1.8° F/minute,
  - 24 - at 570° F for 2 hours,
  - 25 - cool down from 570° F to room temperature within 5 hours.
- 26

27 The Cs/Al-UTD-1 prepared above was further exchanged to make Pt/Cs/Al-  
28 UTD-1. 0.62 Gram of the above Cs/Al-UTD-1 was suspended in 10 g of water.  
29 Pt(NH<sub>3</sub>)<sub>4</sub>Cl<sub>2</sub>·H<sub>2</sub>O (5.6 mg) was added to 6 g water. The resulting Pt solution was  
30 added to the zeolite slurry with hand shaking, and hand shaking continued for three  
31 minutes. Then the suspension was placed on a shaker and shaken at room temperature  
32 for 24 hours. The pH of the suspension was measured and found to be 9.6. The  
33 suspension was filtered without washing with water, and the resulting solid was air  
34 dried at room temperature overnight. The resulting solid was calcined in air with the  
following temperature program:

- 01 - from room temperature to 250° F at a heating rate of 1° F/minute,  
02 - at 250° F for 16 hours,  
03 - from 250° F to 570° F at a heating rate of 1.8°F/minute,  
04 - at 570° F for 2 hours,  
05 - cool down from 570° F to room temperature within 5 hours.

06 The above Pt/Cs/Al-UTD-1 was tested for lack of acidity as follows:

07 The above Pt/Cs/AL-UTD-1 was pretreated in hydrogen flow (300 ml/min.)  
08 using the following temperature program:

- 09 - from room temperature to 400° F at a heating rate of 10° F/minute,  
10 - at 400° F for 30 minutes;  
11 - from 400° F to 900° F at a heating rate of 16.7°F/minute,  
12 - at 900° F for 1 hour,  
13 - cool down to 800° F to start the reaction for the acidity test.

14 All the reactions described below were conducted in a flow-type reactor system  
15 equipped with an on-line capillary GC.

16 The feed used for this test was anhydrous n-octane containing 20 ppm sulfur  
17 (as dimethyl disulfide). The sulfur in the feed was used to poison the Pt species loaded  
18 in the zeolite. After the poisoning was completed, the catalytic activity of Pt species  
19 was reduced to a very low value. It is known that acid-catalyzed cracking reaction will  
20 preferably result in the formation of iso-alkanes such as iso-butane. By contrast, n-  
21 alkanes such as n-butane are the main products of metal-catalyzed cracking reactions.  
22 Based on this background, the acidity (if any) of the catalysts is expressed by using the  
23 ratio of iso-butane to n-butane (i-Bu/n-Bu) produced at a C5 yield of 95% after Pt has  
24 lost its activity. The higher the (i-Bu/n-Bu) ratio, the stronger the acidity.

25 The above Pt/Cs/Al-UTD-1 had an (i-Bu/n-Bu) ratio of 0.03, which is very low  
26 and reveals the complete neutralization of acid sites by Cs species in this catalysts.

27 The reaction temperature was adjusted to 930° F to obtain a C5+ yield of 95%.  
28 Other reaction parameters were: pressure = 200 psig and WHSV = 3 h<sup>-1</sup>.

29 Through this reaction, the catalyst was also sulfided for the reforming screening  
30 to be described below.

01

02

Example 9

03

## Reforming Using Pt/Cs/Al-UTD-1

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Immediately after the acidity test described above, the sulfided Pt/Cs/Al-UTD-1 was screened in the same reactor system for reforming. A 300° F end point naphtha was used as feed and its composition is listed below. The reactions were performed at pressure = 130 psig and WHSV = 3 per hour. The reaction temperature was varied between 930 and 980° F. Results are listed below:

	wt.-% in Feed	Yield, wt.-% at 930° F	Yield, wt.-% at 980° F
methane	0	0.25	0.81
ethane	0	0.37	1.74
propane	0.01	0.57	2.18
butanes	0.11	0.64	1.77
pentenes	1.20	1.42	2.18
hexanes	7.61	4.75	4.85
benzene	0.37	1.36	1.44
toluene	4.03	8.32	8.77
EB + xylenes	8.14	14.77	16.66
C9 aromatics	0.23	1.77	2.82
C7-C9 sats	74.57	3.66	2.31
unknowns	3.73	5.14	7.21
C5+ total	99.88	97.12	92.26

31

32

Example 10

33

34

The Spaciousness Index (SI) is defined as the yield ratio of iso-butane and n-butane in hydrocracking of a C10-cycloalkane such as n-butylcyclohexane over bifunctional zeolites or other molecular sieve materials. The ratio increases with increasing pore size and is, therefore, a valuable tool for characterizing the shape selective properties

01 of molecular sieve materials. Based on the results of a variation of nature and amount  
02 of the noble metal exchanged into the acid zeolites, the use of Pd as hydrogenation/  
03 dehydrogenation component is recommended. The optimum Pd loading is around 0.27  
04 wt.%. In addition, experimental data reveal that the Spaciousness Index (SI) is under  
05 certain circumstances independent of (i) the reaction temperature, (ii) the Si/Al ratio of  
06 zeolite and (iii) the crystal size. Hence, it represents a characteristic constant for a  
07 given zeolite.  
08

09

10 There are several publications on the Spaciousness Index (SI). The main two  
11 references are:  
12

13

14 (i) J. Weitkamp, S. Ernst and R. Kumar, Appl. Catal. 27 (1986) 207-210.

15 (ii) J. Weitkamp, S. Ernst and C.Y. Chen, in "Zeolites: Facts, Figures, Future", pp.

16 1115 - 1129, Proceedings of the 8th International Zeolite Conference, Amsterdam,

17 The Netherlands, July 10-14, 1989, Studies in Surface Science and Catalysis, Vol.

18 49, edited by P.A. Jacobs and R.A. van Santen, Publisher: Elsevier, Amsterdam -

19 Oxford - New York - Tokyo, 1989.  
20

21

22 For the determination of the Spaciousness Index, Pd/Al-UTD-1 (0.27 wt.% Pd) was  
23 pretreated in hydrogen flow (300 ml/min.) using the following temperature program:

24

25 - from room temperature to 660° F at a heating rate of 2°F/minute,

26 - at 660° F for 10 hours,

27 - cool down to certain reaction temperature (e.g., 480° F) to start the

28 determination of the Spaciousness Index.  
29

30

31 The reactions were performed at pressure = 130 psig and WHSV = 3 h<sup>-1</sup>. The reaction  
32 temperature was varied between 430 and 660° F. n-Butylcyclohexane was used as  
33 feed.  
34

Based on the results, it was determined that the Pd/Al-UTD-1 has a Spaciousness Index of 11.5, where the yield of hydrocracking products ranges between 15 and 65 %.

1 In the literature, the following values of the SI are reported for various zeolites: 21.0  
2 (Y), 20.5 (ZSM-20), 19.0 (Beta), 17.0 (L), 12.5 (ZSM-25), 7.5 (mordenite), 5.0 (EU-  
3 1 and offretite), 4.0 (SAPO-5), 3.0 (ZSM-12) and 1.0 (ZSM-5/-11/-22/-23).  
4 According to the above SI values, the effective pore size of the Pd/Al-UTD-1 is  
5 smaller than the effective diameter of the largest voids in Y, ZSM-20, beta and L but  
6 larger than those of other one-dimensional 12-membered ring zeolites.

7

8

Example 11

9

## Pt- Containing All-Silica UTD-1 Constraint Index

10

A sample of all-silica UTD-1 was prepared in a manner similar to that described  
11 in U. S. Patent No. 5,489,424. It was calcined and analyzed by X-ray diffraction and  
12 the results are tabulated in Table V below

13

TABLE V

14

Calcined All-silica UTD-1

<u>2 Theta</u>	<u>d</u>	<u>Relative Intensity</u>
5.938	14.87	100
7.559	11.69	56.8
9.233	9.57	5.6
10.318	8.57	1.3
14.432	6.13	6.5
18.069	4.91	6.2
19.703	4.50	10.0
20.149	4.40	3.0
21.002	4.23	26.4
21.861	4.06	5.4
22.398	3.97	3.1
23.035	3.86	2.5
24.220	3.67	7.1
24.886	3.58	5.7
26.093	3.41	3.2
28.131	3.17	2.1

-37-

<u>2 Theta</u>	<u>d</u>	<u>Relative Intensity</u>
29.784	3.00	2.1
32.257	2.77	2.3

1

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11

The sample was platinum exchanged in a manner similar to that described in Example 7 (nominal loading of Pt 0.5 wt%) and calcined. The Constraint Index of the resulting material was determined using the procedure of Example 6 at 800°F. After ten minutes, the conversion was about 10%. A spectrum of aromatics was made with the following ratios:

Benzene	2.45
Toluene	1.00
Xylenes	1.75
C <sub>9</sub> and higher	2.80

## 01 WHAT IS CLAIMED IS:

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1. An aluminosilicate zeolite having a silica/alumina mole ratio of about 500 or less, having pores with at least one cross-sectional dimension greater than 7.5 Angstroms.

2. A zeolite comprising a first oxide selected from the group consisting of silicon oxide, germanium oxide and mixtures thereof and a second oxide selected from the group consisting of aluminum oxide, gallium oxide, iron oxide, indium oxide and mixtures of aluminum oxide, boron oxide, gallium oxide, iron oxide, indium oxide, titanium oxide, and vanadium oxide, said zeolite having, after calcination, the X-ray diffraction lines of Table I, and having a mole ratio of the first oxide to the second oxide of about 500 or less.

3. A zeolite according to Claim 2 wherein the oxides comprise silicon oxide and aluminum oxide.

4. A zeolite according to Claim 2 wherein said zeolite is predominantly in the hydrogen form.

5. A zeolite according to Claim 2 made substantially free of acidity by neutralizing said zeolite with a basic metal.

6. A zeolite according to Claim 2 having a crystallite size, as estimated by TEM along the C axis, of about 2000 Å or less.

7. A zeolite according to Claim 6 wherein the crystallite size is about 500 to 1000 Å.



- 01 8. A method of preparing a boron-containing zeolite comprising oxides of boron  
02 and silica, said zeolite having, after calcination, the X-ray diffraction lines of  
03 Table I, said method comprising:  
04  
05 (a) preparing an aqueous solution containing calcined boron-containing Beta  
06 zeolite, an alkali metal or alkaline earth metal cation, and a  
07 bis(pentamethylcyclopentadienyl) cobalt (III) ion having an anionic  
08 counterion which is not detrimental to the formation of the boron-  
09 containing zeolite;  
10  
11 (b) maintaining the aqueous solution under conditions sufficient to form  
12 crystals of the boron-containing zeolite; and  
13 (c) recovering crystals of the boron-containing zeolite.  
14
- 15 9. A process for converting hydrocarbons comprising contacting a  
16 hydrocarbonaceous feed at hydrocarbon converting conditions with a catalyst  
17 comprising a zeolite comprising a first oxide selected from the group consisting  
18 of silicon oxide, germanium oxide and mixtures thereof and a second oxide  
19 selected from the group consisting of aluminum oxide, gallium oxide, iron oxide,  
20 indium oxide and mixtures of aluminum oxide, boron oxide, gallium oxide, iron  
21 oxide, indium oxide, titanium oxide, and vanadium oxide, said zeolite having,  
22 after calcination, the X-ray diffraction lines of Table I, and having a mole ratio of  
23 the first oxide to the second oxide of about 500 or less.  
24  
25  
26
- 27 10. The process of Claim 9 wherein the zeolite is predominantly in the hydrogen  
28 form.  
29
- 30 11. The process of Claim 9 wherein the process is a hydrocracking process  
31 comprising contacting a hydrocarbon feedstock under hydrocracking conditions  
32 with a catalyst comprising a zeolite comprising a first oxide selected from the  
33 group consisting of silicon oxide, germanium oxide and mixtures thereof and a  
34 second oxide selected from the group consisting of aluminum oxide, gallium  
oxide, iron oxide, indium oxide and mixtures of aluminum oxide, boron oxide,

- 01 gallium oxide, iron oxide, indium oxide, titanium oxide, and vanadium oxide,  
02 said zeolite having, after calcination, the X-ray diffraction lines of Table I, and  
03 having a mole ratio of the first oxide to the second oxide of about 500 or less.  
04
- 05 12. The process of Claim 11 wherein the zeolite is predominantly in the hydrogen  
06 form.  
07  
08
- 09 13. The process of Claim 9 wherein the process is a dewaxing process comprising  
10 contacting a hydrocarbon feedstock under dewaxing conditions with a catalyst  
11 comprising a zeolite comprising a first oxide selected from the group consisting  
12 of silicon oxide, germanium oxide and mixtures thereof and a second oxide  
13 selected from the group consisting of aluminum oxide, gallium oxide, iron oxide,  
14 indium oxide and mixtures of aluminum oxide, boron oxide, gallium oxide, iron  
15 oxide, indium oxide, titanium oxide, and vanadium oxide, said zeolite having,  
16 after calcination, the X-ray diffraction lines of Table I, and having a mole ratio of  
17 the first oxide to the second oxide of about 500 or less.  
18  
19  
20
- 21 14. The process of Claim 13 wherein the zeolite is predominantly in the hydrogen  
22 form.  
23  
24
- 25 15. The process of Claim 9 wherein the process is a process for improving the  
26 viscosity index of the dewaxed product of waxy hydrocarbon feeds comprising  
27 contacting the waxy hydrocarbon feed under isomerization dewaxing conditions  
28 with a catalyst comprising a zeolite comprising a first oxide selected from the  
29 group consisting of silicon oxide, germanium oxide and mixtures thereof and a  
30 second oxide selected from the group consisting of aluminum oxide, gallium  
31 oxide, iron oxide, indium oxide and mixtures of aluminum oxide, boron oxide,  
32 gallium oxide, iron oxide, indium oxide, titanium oxide, and vanadium oxide,  
33 said zeolite having, after calcination, the X-ray diffraction lines of Table I, and  
34 having a mole ratio of the first oxide to the second oxide of about 500 or less.

- 01 16. The process of Claim 15 wherein the zeolite is predominantly in the hydrogen  
02 form.  
03
- 04 17. The process of Claim 9 wherein the process is a process for producing a C<sub>20+</sub>  
05 lube oil from a C<sub>20+</sub> olefin feed comprising isomerizing said olefin feed over a  
06 catalyst comprising at least one Group VIII metal and a zeolite comprising a first  
07 oxide selected from the group consisting of silicon oxide, germanium oxide and  
08 mixtures thereof and a second oxide selected from the group consisting of  
09 aluminum oxide, gallium oxide, iron oxide, indium oxide and mixtures of  
10 aluminum oxide, boron oxide, gallium oxide, iron oxide, indium oxide, titanium  
11 oxide, and vanadium oxide, said zeolite having, after calcination, the X-ray  
12 diffraction lines of Table I, and having a mole ratio of the first oxide to the  
13 second oxide of about 500 or less.  
14  
15  
16
- 17 18. The process of Claim 17 wherein the zeolite is predominantly in the hydrogen  
18 form.  
19  
20
- 21 19. The process of Claim 9 wherein the process is a process for catalytically  
22 dewaxing a hydrocarbon oil feedstock boiling above about 350°F and containing  
23 straight chain and slightly branched chain hydrocarbons comprising contacting  
24 said hydrocarbon oil feedstock in the presence of added hydrogen gas at a  
25 hydrogen pressure of about 15-3000 psi with a catalyst comprising at least one  
26 Group VIII metal and a zeolite comprising a first oxide selected from the group  
27 consisting of silicon oxide, germanium oxide and mixtures thereof and a second  
28 oxide selected from the group consisting of aluminum oxide, gallium oxide, iron  
29 oxide, indium oxide and mixtures of aluminum oxide, boron oxide, gallium  
30 oxide, iron oxide, indium oxide, titanium oxide, and vanadium oxide, said zeolite  
31 having, after calcination, the X-ray diffraction lines of Table I, and having a mole  
32 ratio of the first oxide to the second oxide of about 500 or less.  
33  
34

- 01 20. The process of Claim 19 wherein the zeolite is predominantly in the hydrogen  
02 form.  
03
- 04 21. The process according to Claim 19 wherein said catalyst comprises a layered  
05 catalyst comprising a first layer comprising at least one Group VIII metal and a  
06 zeolite comprising a first oxide selected from the group consisting of silicon  
07 oxide, germanium oxide and mixtures thereof and a second oxide selected from  
08 the group consisting of aluminum oxide, gallium oxide, iron oxide, indium oxide  
09 and mixtures of aluminum oxide, boron oxide, gallium oxide, iron oxide, indium  
10 oxide, titanium oxide, and vanadium oxide, said zeolite having, after calcination,  
11 the X-ray diffraction lines of Table I, and having a mole ratio of the first oxide to  
12 the second oxide of about 500 or less, and a second layer comprising an  
13 aluminosilicate zeolite which is more shape selective than the zeolite of said first  
14 layer.  
15  
16  
17
- 18 22. The process of Claim 9 wherein the process is a process for preparing a  
19 lubricating oil which comprises:  
20  
21  
22 hydrocracking in a hydrocracking zone a hydrocarbonaceous feedstock to obtain  
23 an effluent comprising a hydrocracked oil; and  
24  
25  
26 catalytically dewaxing said effluent comprising hydrocracked oil at a temperature  
27 of at least about 400°F and at a pressure of from about 15 psig to about 3000  
28 psig in the presence of added hydrogen gas with a catalyst comprising at least  
29 one Group VIII metal and a zeolite comprising a first oxide selected from the  
30 group consisting of silicon oxide, germanium oxide and mixtures thereof and a  
31 second oxide selected from the group consisting of aluminum oxide, gallium  
32 oxide, iron oxide, indium oxide and mixtures of aluminum oxide, boron oxide,  
33 gallium oxide, iron oxide, indium oxide, titanium oxide, and vanadium oxide,  
34 said zeolite having, after calcination, the X-ray diffraction lines of Table I, and  
having a mole ratio of the first oxide to the second oxide of about 500 or less.

- 01  
02 23. The process of Claim 22 wherein the zeolite is predominantly in the hydrogen  
03 form.  
04  
05  
06 24. The process of Claim 9 wherein the process is a process for isomerization  
07 dewaxing a raffinate comprising contacting said raffinate in the presence of  
08 added hydrogen with a catalyst comprising at least one Group VIII metal and a  
09 zeolite comprising a first oxide selected from the group consisting of silicon  
10 oxide, germanium oxide and mixtures thereof and a second oxide selected from  
11 the group consisting of aluminum oxide, gallium oxide, iron oxide, indium oxide  
12 and mixtures of aluminum oxide, boron oxide, gallium oxide, iron oxide, indium  
13 oxide, titanium oxide, and vanadium oxide, said zeolite having, after calcination,  
14 the X-ray diffraction lines of Table I, and having a mole ratio of the first oxide to  
15 the second oxide of about 500 or less.  
16  
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18  
19 25. The process of Claim 24 wherein the zeolite is predominantly in the hydrogen  
20 form.  
21  
22 26. The process of Claim 24 wherein the raffinate is bright stock.  
23  
24  
25 27. The process of Claim 9 wherein the process is a process for increasing the octane  
26 of a hydrocarbon feedstock to produce a product having an increased aromatics  
27 content comprising contacting a hydrocarbonaceous feedstock which comprises  
28 normal and slightly branched hydrocarbons having a boiling range above about  
29 40°C and less than about 200°C, under aromatic conversion conditions with a  
30 catalyst comprising a zeolite comprising a first oxide selected from the group  
31 consisting of silicon oxide, germanium oxide and mixtures thereof and a second  
32 oxide selected from the group consisting of aluminum oxide, gallium oxide, iron  
33 oxide, indium oxide and mixtures of aluminum oxide, boron oxide, gallium  
34 oxide, iron oxide, indium oxide, titanium oxide, and vanadium oxide, said zeolite

- 01       having, after calcination, the X-ray diffraction lines of Table I, and having a mole  
02       ratio of the first oxide to the second oxide of about 500 or less.  
03  
04       28.   The process of Claim 27 wherein the zeolite is substantially free of acidity.  
05  
06  
07       29.   The process of Claim 27 wherein the zeolite contains a Group VIII metal  
08       component.  
09  
10       30.   The process of Claim 9 wherein the process is a catalytic cracking process  
11       comprising contacting a hydrocarbon feedstock in a reaction zone under catalytic  
12       cracking conditions in the absence of added hydrogen with a catalyst comprising  
13       a zeolite comprising a first oxide selected from the group consisting of silicon  
14       oxide, germanium oxide and mixtures thereof and a second oxide selected from  
15       the group consisting of aluminum oxide, gallium oxide, iron oxide, indium oxide  
16       and mixtures of aluminum oxide, boron oxide, gallium oxide, iron oxide, indium  
17       oxide, titanium oxide, and vanadium oxide, said zeolite having, after calcination,  
18       the X-ray diffraction lines of Table I, and having a mole ratio of the first oxide to  
19       the second oxide of about 500 or less.  
20  
21  
22  
23       31.   The process of Claim 30 wherein the zeolite is predominantly in the hydrogen  
24       form.  
25  
26  
27       32.   The process of Claim 30 wherein the catalyst additionally comprises a large pore  
28       crystalline cracking component.  
29  
30  
31       33.   The process of Claim 9 wherein the process is an isomerization process for  
32       isomerizing C<sub>4</sub> to C<sub>7</sub> hydrocarbons, comprising contacting a catalyst, comprising  
33       at least one Group VIII metal impregnated on a zeolite comprising a first oxide  
34       selected from the group consisting of silicon oxide, germanium oxide and  
      mixtures thereof and a second oxide selected from the group consisting of  
      aluminum oxide, gallium oxide, iron oxide, indium oxide and mixtures of

- 01 aluminum oxide, boron oxide, gallium oxide, iron oxide, indium oxide, titanium  
02 oxide, and vanadium oxide, said zeolite having, after calcination, the X-ray  
03 diffraction lines of Table I, and having a mole ratio of the first oxide to the  
04 second oxide of about 500 or less, with a feed having normal and slightly  
05 branched C<sub>4</sub> to C<sub>7</sub> hydrocarbons under isomerizing conditions.  
06  
07
- 08 34. The process of Claim 33 wherein the zeolite is predominantly in the hydrogen  
09 form.  
10
- 11 35. The process of Claim 33 wherein the catalyst has been calcined in a steam/air  
12 mixture at an elevated temperature after impregnation of the Group VIII metal.  
13  
14
- 15 36. The process of Claim 33 wherein the Group VIII metal is platinum.  
16
- 17 37. The process of Claim 9 wherein the process is a process for alkylating an  
18 aromatic hydrocarbon which comprises contacting under alkylation conditions at  
19 least a mole excess of an aromatic hydrocarbon with a C<sub>2</sub> to C<sub>20</sub> olefin under at  
20 least partial liquid phase conditions and in the presence of a catalyst comprising a  
21 zeolite comprising a first oxide selected from the group consisting of silicon  
22 oxide, germanium oxide and mixtures thereof and a second oxide selected from  
23 the group consisting of aluminum oxide, gallium oxide, iron oxide, indium oxide  
24 and mixtures of aluminum oxide, boron oxide, gallium oxide, iron oxide, indium  
25 oxide, titanium oxide, and vanadium oxide, said zeolite having, after calcination,  
26 the X-ray diffraction lines of Table I, and having a mole ratio of the first oxide to  
27 the second oxide of about 500 or less.  
28  
29  
30
- 31 38. The process of Claim 37 wherein the olefin is a C<sub>2</sub> to C<sub>4</sub> olefin.  
32  
33
- 34 39. The process of Claim 37 wherein the aromatic hydrocarbon and olefin are  
present in a molar ratio of about 4:1 to about 20:1, respectively.

- 01 40. The process of Claim 37 wherein the aromatic hydrocarbon is selected from the  
02 group consisting of benzene, toluene, xylene, or mixtures thereof.  
03
- 04 41. The process of Claim 37 wherein the zeolite is predominantly in the hydrogen  
05 form.  
06  
07
- 08 42. The process of Claim 9 wherein the process is a process for transalkylating an  
09 aromatic hydrocarbon which comprises contacting under transalkylating  
10 conditions an aromatic hydrocarbon with a polyalkyl aromatic hydrocarbon  
11 under at least partial liquid phase conditions and in the presence of a catalyst  
12 comprising a zeolite comprising a first oxide selected from the group consisting  
13 of silicon oxide, germanium oxide and mixtures thereof and a second oxide  
14 selected from the group consisting of aluminum oxide, gallium oxide, iron oxide,  
15 indium oxide and mixtures of aluminum oxide, boron oxide, gallium oxide, iron  
16 oxide, indium oxide, titanium oxide, and vanadium oxide, said zeolite having,  
17 after calcination, the X-ray diffraction lines of Table I, and having a mole ratio of  
18 the first oxide to the second oxide of about 500 or less.  
19  
20  
21
- 22 43. The process of Claim 42 wherein the aromatic hydrocarbon and the polyalkyl  
23 aromatic hydrocarbon are present in a molar ratio of from about 1:1 to about  
24 25:1, respectively.  
25  
26
- 27 44. The process of Claim 42 wherein the aromatic hydrocarbon is a member selected  
28 from the group consisting of benzene, toluene, xylene, or mixtures thereof.  
29
- 30 45. The process of Claim 42 wherein the polyalkyl aromatic hydrocarbon is a  
31 dialkylbenzene.  
32  
33
- 34 46. The process of Claim 42 wherein the zeolite is predominantly in the hydrogen  
form.



- 01 47. The process of Claim 9 wherein the process is a process to convert paraffins to  
02 aromatics which comprises contacting paraffins with a catalyst comprising  
03 gallium, zinc, or a compound of gallium or zinc and a zeolite comprising a first  
04 oxide selected from the group consisting of silicon oxide, germanium oxide and  
05 mixtures thereof and a second oxide selected from the group consisting of  
06 aluminum oxide, gallium oxide, iron oxide, indium oxide and mixtures of  
07 aluminum oxide, boron oxide, gallium oxide, iron oxide, indium oxide, titanium  
08 oxide, and vanadium oxide, said zeolite having, after calcination, the X-ray  
09 diffraction lines of Table I, and having a mole ratio of the first oxide to the  
10 second oxide of about 500 or less.  
11  
12  
13
- 14 48. The process according to Claim 47 wherein the zeolite is substantially free of  
15 acidity.  
16
- 17 49. The process of Claim 9 wherein the process is a process for isomerizing olefins  
18 comprising contacting said olefin under conditions which cause isomerization of  
19 the olefin with a catalyst comprising a zeolite comprising a first oxide selected  
20 from the group consisting of silicon oxide, germanium oxide and mixtures  
21 thereof and a second oxide selected from the group consisting of aluminum  
22 oxide, gallium oxide, iron oxide, indium oxide and mixtures of aluminum oxide,  
23 boron oxide, gallium oxide, iron oxide, indium oxide, titanium oxide, and  
24 vanadium oxide, said zeolite having, after calcination, the X-ray diffraction lines  
25 of Table I, and having a mole ratio of the first oxide to the second oxide of about  
26 500 or less.  
27  
28  
29
- 30 50. The process according to Claim 49 wherein the zeolite is predominantly in the  
31 hydrogen form.  
32  
33
- 34 51. The process of Claim 9 wherein the process is a process for isomerizing an  
isomerization feed comprising an aromatic C<sub>8</sub> stream of xylene isomers or  
mixtures of xylene isomers and ethylbenzene, wherein a more nearly equilibrium

01 ratio of ortho-, meta and para-xylenes is obtained, said process comprising  
02 contacting said feed under isomerization conditions with a catalyst comprising a  
03 zeolite comprising a first oxide selected from the group consisting of silicon  
04 oxide, germanium oxide and mixtures thereof and a second oxide selected from  
05 the group consisting of aluminum oxide, gallium oxide, iron oxide, indium oxide  
06 and mixtures of aluminum oxide, boron oxide, gallium oxide, iron oxide, indium  
07 oxide, titanium oxide, and vanadium oxide, said zeolite having, after calcination,  
08 the X-ray diffraction lines of Table I, and having a mole ratio of the first oxide to  
09 the second oxide of about 500 or less.  
10  
11

12  
13 52. The process of Claim 51 wherein the zeolite is predominantly in the hydrogen  
14 form.  
15

16 53. The process of Claim 9 wherein the process is a process for oligomerizing olefins  
17 comprising contacting an olefin feed under oligomerization conditions with a  
18 catalyst comprising a zeolite comprising a first oxide selected from the group  
19 consisting of silicon oxide, germanium oxide and mixtures thereof and a second  
20 oxide selected from the group consisting of aluminum oxide, gallium oxide, iron  
21 oxide, indium oxide and mixtures of aluminum oxide, boron oxide, gallium  
22 oxide, iron oxide, indium oxide, titanium oxide, and vanadium oxide, said zeolite  
23 having, after calcination, the X-ray diffraction lines of Table I, and having a mole  
24 ratio of the first oxide to the second oxide of about 500 or less.  
25  
26  
27

28 54. The process of Claim 53 wherein the zeolite is predominantly in the hydrogen  
29 form.  
30

31  
32 55. A process for converting lower alcohols and other oxygenated hydrocarbons  
33 comprising contacting said lower alcohol or other oxygenated hydrocarbon  
34 under conditions to produce liquid products with a catalyst comprising a zeolite  
comprising a first oxide selected from the group consisting of silicon oxide,  
germanium oxide and mixtures thereof and a second oxide selected from the

- 01 group consisting of aluminum oxide, gallium oxide, iron oxide, indium oxide and  
02 mixtures of aluminum oxide, boron oxide, gallium oxide, iron oxide, indium  
03 oxide, titanium oxide, and vanadium oxide, said zeolite having, after calcination,  
04 the X-ray diffraction lines of Table I, and having a mole ratio of the first oxide to  
05 the second oxide of about 500 or less.  
06  
07
- 08 56. The process according to Claim 55 wherein the zeolite is predominantly in the  
09 hydrogen form.  
10
- 11  
12 57. In a process for the reduction of oxides of nitrogen contained in a gas stream in  
13 the presence of oxygen wherein said process comprises contacting the gas  
14 stream with a zeolite, the improvement comprising using as the zeolite a zeolite  
15 comprising a first oxide selected from the group consisting of silicon oxide,  
16 germanium oxide and mixtures thereof and a second oxide selected from the  
17 group consisting of aluminum oxide, gallium oxide, iron oxide, indium oxide and  
18 mixtures of aluminum oxide, boron oxide, gallium oxide, iron oxide, indium  
19 oxide, titanium oxide, and vanadium oxide, said zeolite having, after calcination,  
20 the X-ray diffraction lines of Table I, and having a mole ratio of the first oxide to  
21 the second oxide of about 500 or less.  
22  
23
- 24  
25 58. The process of Claim 57 wherein said zeolite contains a metal or metal ions  
26 capable of catalyzing the reduction of the oxides of nitrogen.  
27
- 28 59. The process of Claim 58 wherein the metal is copper, cobalt or mixtures thereof.  
29
- 30  
31 60. The process of Claim 58 wherein the gas stream is the exhaust stream of an  
32 internal combustion engine.  
33
- 34 61. A process for converting hydrocarbons comprising contacting a  
hydrocarbonaceous feed at hydrocarbon converting conditions with a catalyst

01 comprising a Group VIII metal and a silica zeolite having, after calcination, the  
02 X-ray diffraction lines of Table 1A.  
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